

TITLE OF THE INVENTION

INK FOR APPLYING A DECORATION ON A MOLDED ARTICLE  
SIMULTANEOUSLY WITH MOLDING, AND DECORATED FILM OR SHEET

BACKGROUND OF THE INVENTION

5       The present invention relates generally to an ink used for applying a decoration on a molded article upon injection molding or the like, and more particularly to a metal powder-containing ink.

For the decoration of the surface of a molded article of  
10      synthetic resin, there is known a method wherein the synthetic resin is injected into a mold cavity provided with a film or sheet having a decoration pre-printed thereon by an ink to integrate the pattern printed on the decorated sheet into the synthetic resin.

15      This method enables the pattern to be formed on a molded article configured such that difficulty is involved in forming a pattern directly on its surface by means of printing. The method have also additional advantages of having higher adhesion strength than could be achieved by  
20      printing on the surface of the molded article and being unlikely to deteriorate with the lapse of years, and so is used for the decorations of the surfaces of various devices inclusive of electronic devices of small size such as portable telephones, and personal computers.

25      In an injection molding process, the decorated sheet with a decoration already printed thereon is first placed in the mold, and a molding synthetic resin melt is then injected into the mold. Since the melt having a temperature of 200°C

to 300°C is injected under high pressure into the mold, however, there are several problems such as a flow of the pattern printed on the decorated sheet, and deformation of the decorated sheet. These problems result in molded article products that are poor in quality or of no commercial value. In some case, the adhesion strength of the decorated sheet to the molded synthetic resin becomes insufficient due to the rolling of the decoration.

To solve such problems, it has been proposed to change the position of a gate of the mold used for injection molding or vary the spacing between the gate and the decorated film or sheet. However, these proposals are found to have another problem that the amount of material wastefully consumed during molding increases.

It has also been proposed to make use of an ink having the nature of extending following the deformation of the decorated film or sheet, which occurs while the synthetic resin melt flows. For this ink, a two-part type of printing ink for intermolecular crosslinking is used, and for a printing ink of high heat resistance, a printing ink containing a thermoplastic aromatic polycarbonate has already been proposed in Patent No. 2997636.

However, even these printing inks are found to flow in severe injection molding conditions such as high injection speeds of synthetic resin melts.

This printing ink flow problem becomes noticeable in the case of a printing ink containing metal particles such as aluminum particles.

The metal particles such as aluminum particles are widely used for the purpose of adding a metallic luster and a high degree of concealing effect to molded articles, and so a grave problem arises in association with a decorated film or sheet with a decoration printed thereon by a printing ink containing metal particles such as aluminum particles.

An object of the present invention is to provide a printing ink containing metal particles, which can prevent any flow of a pattern printed on a decorated film or sheet that is placed in a mold for injection molding while it is integrated with synthetic resin, thereby foreclosing the possibility of yielding defectives on injection molding.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a plan representation of an injection molded sample prepared in the example according to the present invention.

#### SUMMARY OF THE INVENTION

According to the present invention, the aforesaid object is achievable by the provision of AN ink used for printing of a preprinted film or sheet used for decorating a molded article by integration with a synthetic resin melt at a synthetic resin molding step, comprising:

a binder comprising a polycarbonate resin, and  
a metal particle coated on the surface thereof with a  
coupling agent or a synthetic resin.

Preferably in this aspect of the present invention, the metal particle is a flat form of aluminum particle, which may

have, or may have not, been coated on its surface with an acrylic resin.

The present invention also provides a printed film or sheet used for decorating a molded article by integration 5 with a synthetic resin melt at a synthetic resin molding step, which has been obtained by printing a synthetic resin film with an ink comprising a binder comprising a polycarbonate resin and a metal particle coated on the surface thereof with a coupling agent or a synthetic resin.

10 Further, the present invention provides a synthetic resin injection molding method wherein a printed film or sheet is prepared by printing using an ink containing a metal particle coated on the surface thereof with a coupling agent or a synthetic resin, the printed film or sheet is then 15 placed in a metal mold, and a synthetic resin melt is finally subjected to injection molding at a temperature of 200°C or higher.

#### DESCRIPTION OF THE PREFERRED EMBODIMENT

According to the present invention, it has now been 20 found that when injection molding is carried out while a sheet with a decoration printed thereon using a ink containing fine metal particles, e.g., a so-called silver ink, is placed in a mold, any flowing of the decorative image applied on the printed film or sheet is prevented by using 25 metal particles coated on their surfaces with a coupling agent or a synthetic resin as the fine metal particles while the image is not adversely affected by a resin melt injected into the mold.

In consideration of the facts that the flowing of the decoration during injection molding does not only relate to the heat resistance, etc. of a binder contained in the ink but also depends largely on fine metal particles contained in  
5 the ink such as the silver ink, the inventors have found that problems such as a decoration flowing problem can be substantially solved by using metal particles treated on their surfaces with a synthetic resin, etc.

For the fine metal particles to be added to inks, flat  
10 fine particles such as scaly ones are used for the purposes of achieving an enhanced concealing effect and obtaining a metallic luster. The present invention takes chief aim at preventing any flowing of the decoration or the like by previously coating the surfaces of these fine metal particles  
15 with a coupling agent or a synthetic resin.

Although why any flowing of the decoration or the like can be prevented by the method of the present invention has yet to be clarified, a possible explanation could be that in  
20 the metal surface coated with the coupling agent or synthetic resin, the affinity of the metal surface for the binder in the ink is so enhanced that the metal surface is less susceptible to influences by a flow of the synthetic resin melt injected during injection molding.

For the binder used with the picture applying ink  
25 according to the present invention, it is preferable to use polycarbonate resins of high heat resistance. For instance, it is acceptable to make use of generally known polycarbonate resins as well as aromatic polycarbonate resins modified by

copolymers comprising 2,2-bis(4-hydroxyphenyl)propane units and 2,2-bis(4-hydroxy-3-methylphenyl)propane units or dialkylsiloxane units.

To be more specific, Yupiron FPC2136 (copol(2,2-bis(4-hydroxyphenyl)propane/2,2-bis(4-hydroxy-3-methylphenyl)propane) carbonate made by Mitsubishi Gas Chemical Company, Inc.), z200 made by the same company, Panlight TS-2020 made by Teijin Limited, and high-heat-resistant thermoplastic resins set forth in Patent No. 2997636 are usable.

For the aluminum particles coated with a synthetic resin or aluminum particles treated with a coupling agent, it is acceptable to use White Silver FZ-7160N, FZ-Q65, FZ-Q95 and 97-2515, all made by Toyo Aluminum Co., Ltd.

The ink of the present invention may be produced by mixing these components with pigments and components generally added to inks, and milling the resultant mixture with the addition of an organic solvent thereto.

As mentioned above, the ink of the present invention is produced by mixing the components together. Alternatively, the present ink may be produced by adding the metal particles treated with the synthetic resin or coupling agent to heat-resistant ink compositions commercially available for the formation of decorated sheets. For instance, it is acceptable to use NORIPHAN HTR (Proell Co., Ltd.) commercially available for the formation of decorated sheets.

The decorated film or sheet produced by use of the ink according to the present invention may be formed by printing

a given pattern on a substrate film such as a polycarbonate film by means of suitable processes such as screen printing.

For the synthetic resin to be integrated with the decorated sheet of the present invention, it is acceptable to  
5 use polycarbonate resins, acrylonitrile·butadiene·styrene copolymers, and polymer alloys comprising polycarbonate resins/acrylonitrile·butadiene·styrene copolymers.

#### EXAMPLE

The present invention is now explained with reference to  
10 some examples.

##### Example 1A

###### Preparation of Ink 1

Twenty (20) parts by weight of a polycarbonate resin (Yuprion **FPC2136** made by Mitsubishi Gas Chemical Company, Inc.), 20 parts by weight of a paste of aluminum particles coated with a synthetic resin (FZ-7160N made by Toyo Aluminum Co., Ltd. with a particle diameter  $D_{50}$  of 13  $\mu\text{m}$ ), 1 part by weight of an anti-foaming agent (BYK-057 made by BYK-Chemie Japan Co., Ltd.), 20 parts by weight of a cyclohexanone solvent, 20 parts by weight of a propylene glycol monomethyl ether acetate solvent and 20 parts by weight of a Solvesso #150 solvent were mixed together, and the resultant mixture was then milled by a rotary mixer into an ink 1.

###### Preparation of Pictured Sheet

25 Using ink 1, a filled-in form of print pattern was formed by screen printing on a polycarbonate resin film of 150 mm x 70 mm in size and 500  $\mu\text{m}$  in thickness. The printed

film was dried at 100°C for 2 hours to prepare a decorated sheet.

#### Injection Molding

The resultant decorated sheet was placed in a mold for  
5 injection molding. Then, a polymer alloy (Yupiron PM1210N  
made by Mitsubishi Gas Chemical Company, Inc.) comprising a  
polycarbonate/acrylonitrile-butadiene-styrene copolymer was  
fed from an injection molding machine with a cylinder  
temperature set at 250°C into the mold at 116 cm<sup>3</sup>/sec. to  
10 prepare an injection molded sample of 1.5 mm in thickness.

#### Measurement of Picture Rolling Amount

In an injection molded sample 1 shown in the plan view  
of Fig. 1, the maximum displacement distance 5 of an image-  
formed area from an end 4 of an area 3 printed by ink 1 on  
15 the decorated sheet 2 was measured. In Table 1, this is  
referred to as the picture rolling amount.

#### Measurement of Peel Strength

The decorated sheet side of the injection molded sample  
was provided with an incision of 1 cm in width, at which the  
20 decorated sheet was peeled from the injection molded resin at  
a rate of pulling of 300 mm/min. to measure a 180° peel  
strength using a tensile tester.

#### Example 1B

The picture rolling amount was measured as in Example 1A  
25 with the exception that a polycarbonate resin (Yupiron S-3000  
made by Mitsubishi Gas Chemical Company, Inc.) for injection  
molding was fed at 116 cm<sup>3</sup>/sec. with a cylinder temperature of  
305°C to prepare an injection molded sample of 1.9 mm in

thickness. The thus measured decoration flowing amount and peel strength are shown in Table 2.

Example 2A

Preparation of Ink 2

5 An ink 2 was prepared as in Example 1A with the exception that a paste of synthetic resin-coated aluminum particles (FZ-Q65 made by Toyo Aluminum Co., Ltd. with a particle diameter  $D_{50}$  of 20  $\mu\text{m}$ ) was used as the aluminum particles.

10 Injection molding was carried out as in Example 1A to prepare an injection molded sample, and the decoration flowing amount and peel strength were thereafter measured with the results shown in Table 1.

Example 2B

15 Injection molding was carried out following Example 1B with the exception that ink 2 was used to prepare an injection molded sample. Then, the decoration flowing amount and peel strength were measured with the results shown in Table 2.

20 Example 3A

Preparation of Ink 3

An ink 3 was prepared as in Example 1A with the exception that a paste of aluminum particles surface-treated with a coupling agent (97-2515 made by Toyo Aluminum Co., Ltd. with a particle diameter  $D_{50}$  of 9  $\mu\text{m}$ ) was used as the aluminum particles.

Injection molding was carried out as in Example 1A to prepare an injection molded sample, and the decoration

flowing amount and peel strength were thereafter measured with the results shown in Table 1.

Example 3B

Injection molding was carried out following Example 1B  
5 with the exception that ink 3 was used to prepare an injection molded sample. Then, the decoration flowing amount and peel strength were measured with the results shown in Table 2.

Comparative Example 1A

10 Preparation of Ink 4

An ink 4 was prepared as in Example 1A with the exception that aluminum particles subjected to no surface treatment (TD280T made by Toyo Aluminum Co., Ltd. with a particle diameter  $D_{50}$  of 20  $\mu\text{m}$ ) was used as the aluminum  
15 particles.

Injection molding was carried out as in Example 1A to prepare an injection molded sample, and the decoration flowing amount and peel strength were thereafter measured with the results shown in Table 1.

20 Comparative Example 1B

Injection molding was carried out following Example 1B with the exception that ink 4 was used to prepare an injection molded sample. Then, the decoration flowing amount and peel strength were measured with the results shown in  
25 Table 2.

Table 1

	Ex. 1A	Ex. 2A	Ex. 3A	Comp. 1A
Decoration Flowing Amount (mm)	1.07	1.02	1.10	4.22
<u>Peel Strength (kN/m)</u>	2.30	2.82	2.51	1.75

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Table 2

	Ex. 1B	Ex. 2B	Ex. 3B	Comp. 1B
Decoration Flowing Amount (mm)	1.54	1.65	1.47	7.5
<u>Peel Strength (kN/m)</u>	2.98	2.96	2.94	1.44

Molded articles obtained while the decorated film or  
10 sheet prepared using the ink of the present invention was  
placed in a mold for injection molding can be reduced in  
terms of the decoration flowing amount due to a flow of the  
synthetic resin during injection. Thus, the present  
invention enables molded article products to be produced in  
15 improved yields.

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